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Corrosion inhibitors for chlorides induced corrosion in reinforced concrete structures

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Abstract

Reinforcements corrosion is the most important cause of premature failure on reinforced concrete structures. Phenomena promoting corrosion are the ingress of chlorides and the reaction of atmospheric CO_2 with cement paste. Aim of this paper is the investigation on the effectiveness of three organic commercial inhibitors in preventing carbon steel chlorides induced corrosion in concrete, since there is not yet a clear knowledge on the real effectiveness of these products. Inhibitors were added to the concrete mixture in dosage suggested by the manufacturers. Chlorides were added in the concrete mixture or penetrated from outside by "ponding" cycles with a 3.5% sodium chloride solution. The effectiveness of the inhibitors has been evaluated by long-term rebar corrosion monitoring in reinforced concrete and by rebar visual inspection after three years tests. Also solution tests were performed in order to verify the effectiveness of inhibition. Results give information about corrosion prevention ability of analysed commercial inhibitors.

Keywords: Concrete (E); Chloride (D); Corrosion (C); Inhibitor

1. Introduction

Carbon steel reinforcements in concrete structures are in passive conditions, that is they are protected by a thin oxide layer promoted by the concrete alkalinity. Corrosion can initiate only when passivity is destroyed. This occurs in two ways: carbonation of concrete, the reaction of atmospheric CO_2 with cement paste, that lowers pH and causes general corrosion; the presence of chlorides at the steel surface in concentration higher than a critical threshold, generally considered in the range of 0.4–1% by cement weight [1,2]. Chlorides may be added to concrete in the mix water or in the aggregates, even if nowadays it is restricted by standards; chlorides can also penetrate from outside, in highway viaducts where de-icing salts are used, or in marine structures. Local passivity destruction by chlorides causes pitting corrosion.

The prevention of reinforcement corrosion is primarily achieved in the design stage by using high quality concrete and adequate cover. Additional prevention methods are adopted when severe environmental conditions occur, or on structures requiring very long service life, as well as in rehabilitation [1].

Among available methods, corrosion inhibitors seem to be attractive because of their low cost and easy handling, compared with other preventive methods [3]. Inhibitors can be divided in two groups: admixed inhibitors, added to fresh concrete for new structures, and migrating inhibitors, which can penetrate into the hardened concrete and are usually proposed in repair system. While admixed inhibitors are commercially available since 70's, migrating corrosion inhibitors for concrete structures were proposed in the last 15–20 years [3]. Nowadays, there are several admixtures available on the market: inorganic compounds based on nitrites, especially used as additives [4–8], and sodium mono–fluoro-phosphate used as migrating inhibitors [9–11]; organic compounds based on mixtures of alkanolamines, amines or amino-acids, or based on an emulsion of unsaturated fatty acid ester of an aliphatic carboxylic acid and a saturated fatty acid, proposed both as admixed and migrating inhibitor [12–22].

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Other non-commercial inhibitors, both inorganic and organic were studied: zinc oxide [23], molibdates and borates [24,25], stannates [26], carboxylate ions, quaternary ammonium salts and many other organic compounds [27–30]. Even if some substances showed good results in solution tests, concerns are with their negative influence on concrete properties, mainly on the setting time, workability and compressive strength.

Nitrite based inhibitors are considered the most effective products available on market: they were studied from 60's both in laboratory and in field tests and several applications confirmed their efficiency. Nitrite acts as a passivator, due to its oxidising properties, and its inhibitive effectiveness is related to the $[NO^-]/[Cl^-]$ molar ratio, that should be higher than 0.8–1 to prevent corrosion [3–8]. Concerns are with their toxicity, solubility and possible increase of corrosion rate in case of low dosage or in the presence of concrete cracks. Controversial results were obtained in severe conditions (cracking of concrete, seawater) [31]; in similar conditions, also some commercial organic products showed low inhibition efficiency [32].

For these reasons in the last 20 years more interest was given to new organic based products. Organic corrosion inhibitors act by adsorption on the metal surface, forming an organic layer, that may inhibit both the anodic and cathodic processes: they are considered mixed inhibitors [16,19,20]. Although a review has been published in 2001 [3], the efficiency of commercial organic corrosion inhibitors is not yet well understood. Laboratory tests showed conflicting results about the inhibiting action of these products, both in solution and in concrete. The lack of a standard procedure to evaluate the effectiveness of these products also makes a very difficult comparison among the different experimentation. In literature, test conditions are not always well defined: the minimum effective inhibitors concentration, or the maximum concrete chloride content are not always reported [33–35]. Moreover, the recent introduction and the very few field applications do not give reliable data on long-term efficiency [3].

This paper illustrates the results of three years research on the inhibitive effectiveness of organic commercial corrosion inhibitors in preventing chlorides induced corrosion. In fact, as reported in [3], there is actually no clear knowledge about the real effectiveness of inhibitors, in particular the effect on time-to-corrosion and on critical chloride threshold. Corrosion was monitored by rebar potential and corrosion rate measurements. Chloride profiles were also measured in concrete subjected to chlorides penetration. Visual observation and weight loss measurements at the end of exposure were carried out. Results are discussed in terms of ability of the corrosion inhibitors to prevent corrosion occurrence or to decrease corrosion rate, once corrosion started.

2. Experimental

Four commercial corrosion inhibitors were tested both in solution and in concrete; three Organic Compound Inhibitor Admixtures (OCIA) and one nitrite based inhibitor (N), only for comparison purposes. The three OCIA are amine-esters (C), aminoalcohols (D) and alkanolamines (E) based.

2.1. Solution tests

Both potentiodynamic and potentiostatic tests were performed in saturated $Ca(OH)_2$ solution, pH = 12.6. Tests were carried out in aerated cells at room temperature (20 ± 2 °C). Samples were obtained from plain carbon steel bars (16 mm in diameter). Tests were carried out on the cross section (200 mm^2 in area), that was polished up to 6 μm diamond paste. As reported in literature [33,36], chlorides level required for occurrence of corrosion is influenced by the sample surface preparation. The polished condition may favour the increase of critical chloride threshold with respect the non-polished surface. But, as all samples were prepared in the same way, a relative comparison may be performed between results obtained in inhibited and not inhibited solution. The lateral surface was coated with an electrical insulator. A wire was welded at the end of the specimen for the electrical connection (Fig. 1a). Inhibitor dosages in solution tests are reported in Table 1.

All the commercial corrosion inhibitors except OCIA-C were completely soluble in the saturated $Ca(OH)_2$ solution. In the presence of OCIA-C (an emulsion unsaturated fatty acid ester of an aliphatic carboxylic acid and a saturated fatty acid) some deposits were observed both on the bottom of the cell and on the carbon steel sample.

Potentiostatic tests were carried out with potentiostat AMEL 1480A. Ten identical carbon steel specimens were polarised at 0 mV SCE in the same cell, connecting them to the potentiostat. Specimens were faced to a saturated calomel reference electrode (SCE) placed in the centre of the cell. An activated titanium wire-net on the bottom of the cell acted as a counter-electrode. After 48 h of passivation in free chlorides conditions, 0.2% chlorides were added every 48 h, up to 3%. The current flowing in each specimen was measured and corrosion has been considered initiated when the anodic current density flowing in the specimen raised above 5 A/m^2. Thereafter, the specimen was disconnected and test continued on the others.

Cathodic potentiodynamic tests were performed in alkaline solution at potential scan rate of 20 mV/min in the cathodic direction, starting from the free corrosion potential until −1.2 V SCE. Inhibitors concentration was the same or double with respect to that used in potentiostatic tests (Table 1). For each of the four inhibitors and the reference solution, three electrochemical tests were carried out.

2.2. Concrete tests

Concrete specimens were cast with cement CEM II A/L 42,5R (European standard CEN ENV 197/1 [37]), water/cement ratio (W/C) equal to 0.5 and calcareous aggregates (10 mm maximum size) from Zandobbio (BG, Italy). Two different concrete mixture were cast: mix 1 with cement content

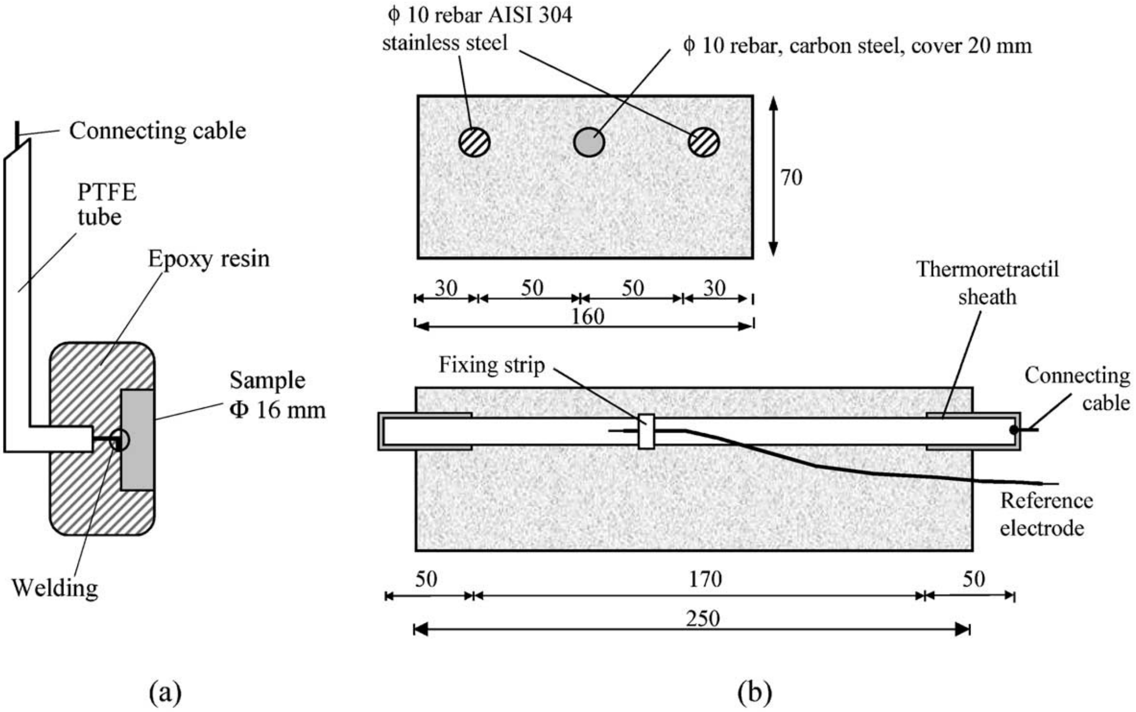

Fig. 1. Solution test specimen (a) and reinforced concrete specimen (b).

300 kg/m^3; mix 2, for higher inhibiting admixture dosage, with cement content 400 kg/m^3. Mixture proportions are reported in Table 2. Concrete samples were cured for 28 days at 20 °C and 95% relative humidity.

A carbon steel rebar was placed in each concrete specimen: 10 mm in diameter and 270 mm length. The ends of each rebar were covered by thermoretractil sheath, so that only a length of 170 mm was exposed to the concrete (Fig. 1b). Two AISI 304 stainless steel rebars (10 mm in diameter) and an AISI 304 stainless steel wire (1 mm diameter) were placed in concrete specimens for corrosion rate measurements. The stainless steel wire (pseudo-reference electrode) was covered by thermoretractil sheath except a little portion (10 mm long) and was fixed by a strip near to carbon steel rebar. Concrete cover was 20 mm.

Inhibitors were added to concrete mixture according to producers recommendations. Two dosages were considered: the recommended dosage for concrete mix 1, and the maximum allowed for concrete mix 2 (Table 1). For each condition, cubic concrete specimens (100 mm in side) were also cast for compressive strength measurements performed after 3 and 28 days of curing: the commercial inhibitors added in the recommended dosages do not influence the mechanical properties (Table 2).

Three series of concrete specimens were cast (Table 3). First series: concrete specimens without and with chlorides 1.5% and 2.5% by cement weight using concrete mix 1, adding inhibitors at the suggested dosages. Second series: concrete specimens with chlorides 1% and 1.5% by cement weight using concrete mix 2, adding inhibitors at the maximum allowed dosages. Third series: concrete specimens cast with concrete mix 1, without admixed chlorides. These specimens were exposed to ponding cycles, i.e. accelerating chlorides penetration, by wetting with 3.5% NaCl solution (1 week) and drying in the laboratory (2 weeks). Two and three concrete specimens were cast for the first two and the third series, respectively.

Table 1
Corrosion inhibitors admixtures: dosages for solution and concrete tests

Inhibitor		Solution (g/L)	Concrete
Nitrite based	Solution (calcium nitrite 29%)	50	7.5 L/m^{3a} 20 L/m^3
OCIA-C (amine-esters)	Liquid	30	5.0 kg/m^{3a} 7.5 kg/m^{3b}
OCIA-D (aminoalcohols)	Liquid	60	10 kg/m^{3a} 16 kg/m^{3b}
OCIA-E (alkanolamines)	Liquid	10	1.6 kg/m^{3a} 4.0 kg/m^{3b}

[a] Dosage suggested by producers.

[b] Maximum allowed dosage.

2.2.1. Corrosion monitoring

Free corrosion potential was measured with respect to a saturated calomel reference electrode (SCE) placed on the

Table 2
Concrete mixture proportions

	Concrete mix 1	Concrete mix 2
Cement content (kg/m^3)	300	400
Water/cement ratio	0.5	0.5
Aggregate content (kg/m^3)	2000	1851
Plasticizer (kg/m^3)	4.5	6
Compressive strength (MPa)^a	47	46

[a] Mean value of concrete without chlorides, with or without inhibitor.

Table 3
Test conditions for reinforced concrete specimens

Series	Concrete mix	Chlorides (% c.w.)	Inhibitor	Dosages
1	Mix 1	0	No	–
			Nitrite based	7.5 L/m^3
				20 L/m^3
			OCIA-C	5 kg/m^3
			OCIA-D	10 kg/m^3
			OCIA-E	1.6 kg/m^3
		1.5	No	–
			Nitrite based	7.5 L/m^3
				20 L/m^3
			OCIA-C	5 kg/m^3
			OCIA-D	10 kg/m^3
			OCIA-E	1.6 kg/m^3
		2.5	No	–
			Nitrite based	7.5 L/m^3
				20 L/m^3
			OCIA-C	5 kg/m^3
			OCIA-D	10 kg/m^3
			OCIA-E	1.6 kg/m^3
2	Mix 2	1	OCIA-C	7.5 kg/m^3
			OCIA-D	16 kg/m^3
			OCIA-E	4 kg/m^3
		1.5	OCIA-C	7.5 kg/m^3
			OCIA-D	16 kg/m^3
			OCIA-E	4 kg/m^3
3	Mix 1	0	No	–
			Nitrite based	7.5 L/m^3
			OCIA-C	5 kg/m^3
			OCIA-D	10 kg/m^3
			OCIA-E	1.6 kg/m^3

concrete surface [38]. Corrosion rate was evaluated through linear polarisation resistance (LPR) method [39,40]. Stainless steel bars were used as counter-electrode, and the stainless steel wire, was used as reference electrode (Fig. 1b). Measurements were carried out by applying a potential scan rate of 10 mV/min from −10 to +10 mV with respect to free corrosion potential [41]. Mean corrosion rate (mA/m^2) was calculated by means of Stern–Geary equation:

$$I_{\mathrm{corr}} = C/R_{\mathrm{p}} \tag{1}$$

where R_{p} is the measured polarisation resistance (Ω m^2) and constant C is assumed equal to 26 mV for active corroding rebars and 52 mV for passive rebars [40]. Mean penetration rate for carbon steel (μm/year) is equal to $1.17 \times I_{\mathrm{corr}}$ (mA/m^2). Since corrosion penetration lower than 1–2 μm/year can be considered negligible [42], polarisation resistance of about 10–20 Ω m^2 is the threshold value below which corrosion is significant.

2.2.2. Visual inspection

At the end of the tests, rebars were extracted from concrete specimens for visual inspection and weight loss measurements. Weight loss has been estimated as the weight per unit length difference between rebars in contact with concrete and uncorroded rebars protected by the sheath. Weight was measured by an analytical balance (0.001 g), and rebar length were measured by a comparator (0.01 mm).

2.2.3. Penetration of chlorides

Chloride profiles were measured both in reinforced concrete specimens and on plain concrete specimens, cast with the same mixture proportions, subjected to chloride penetration. Concrete cores (30 mm in diameter) were drilled from the specimens, then cut into 10 mm slices and were subsequently crushed and dissolved in nitric acid. Total chlorides content were analysed by potentiometric titration with $AgNO_3$ 0.01 N [43].

Chloride penetration in concrete is due to the presence of different mechanisms: mainly diffusion and capillary sorption. Nevertheless, for comparison purposes, experimental profiles may be interpolated using an analytical solution of the second Fick's law of diffusion. Supposing that chlorides concentration at the concrete surface (C_{s}) is constant with time, and considering an effective chlorides diffusion coefficient (D_{ce}) that does not vary with time and space, i.e. concrete is homogeneous, the analytical solution is:

$$\frac{C(x,t)}{C_{\mathrm{s}}} = 1 - erf\left(\frac{x}{2\sqrt{D_{\mathrm{ce}}t}}\right) \tag{2}$$

where $C(x,t)$ is the chloride concentration at the depth x after time t.

After two months of exposure in a controlled atmosphere (80–90% RH), rebars embedded in chlorides free concrete were polarised for 48 h at −500 and −650 mV SCE in order to study the behaviour of the inhibitors under a cathodic polarisation. Embedded reference electrode was used for potential measurements and stainless steel bars as counter-electrode. Rebar potential was measured with an external SCE before and after the polarisation.

3. Results

3.1. Solution tests

Results of potentiostatic tests are reported in Fig. 2 as number of corroded samples as a function of chlorides content. In the non-inhibited solution corrosion occurred on the first sample after the second chloride addition (0.4%). All carbon steel samples corroded for chlorides concentration 0.8%. In the presence of calcium nitrite based inhibitor, corrosion initiated for 80% of the carbon steel samples with chloride concentration in the range of 1–1.4%. Not promising results were obtained with organic inhibitors OCIA-D and OCIA-E: samples corroded for chlorides content similar or slightly higher with respect to results obtained with the reference solution. As reported in [3], this poor effect can be explained due to the fact that the inhibiting agents of these organic inhibitors are volatile amines, so their evaporation is possible if tests cells are not closed (due to the low molecular weight and quite high vapour pressure). Only inhibitor OCIA-C increases critical chlorides concentration; in this case, at the end of the tests, when chloride content reached 3%, corrosion occurred only on three of the ten samples. A possible explanation is that this product is an emulsion organic based inhibitor, so physical adsorption may occur on carbon steel samples that prevent chlorides to be in contact with the metal.

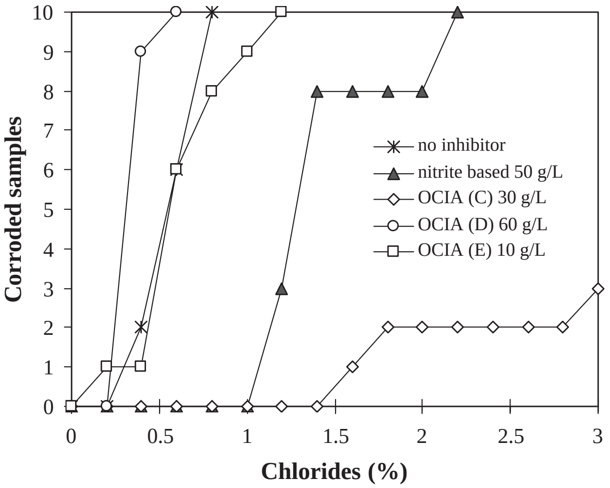

Fig. 2. Potentiostatic tests: number of corroded carbon steel samples as a function of chlorides added to solution.

Potentiodynamic polarisation curves in saturated $Ca(OH)_2$ solution are shown in Fig. 3. Considering the cathodic current density in the potential range of −500/−800 mV SCE, the highest value was measured in solution with nitrite based inhibitor. In solution with OCIA-D and OCIA-E the curves are very similar to that obtained in solution without inhibitor. A lowering of cathodic current density, more pronounced with higher inhibitor dosage, was observed in the presence of OCIA-C. This confirm results obtained in potentiostatic tests with this inhibitor: due to the reduction of limiting current density an increase in critical chlorides content should be expected. The reduction of the limiting current density can be related to the adsorption of the inhibitor on the metal surface.

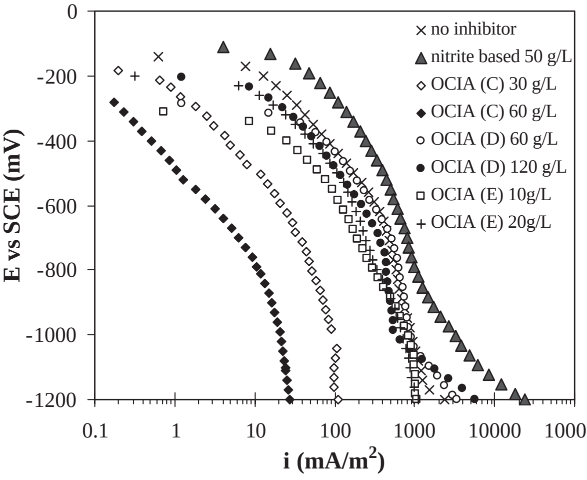

Fig. 3. Cathodic potentiodynamic polarisation curves in saturated $Ca(OH)_2$ solution.

3.2. Chlorides containing concrete

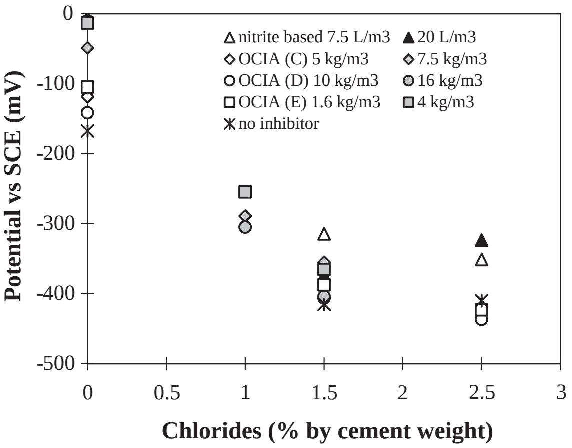

Fig. 4. Rebar free corrosion potential in concrete specimens with admixed chlorides: mean values between 100 and 500 days of atmospheric exposure. Open symbols: inhibitor dosage suggested by producers. Filled symbols: maximum allowed dosage.

Corrosion potential and polarisation resistance measurements are reported in Figs. 4 and 5, respectively. As no significant variations were observed in the measured data, only the mean values are reported. Results showed that rebars in concrete without chlorides are in passive conditions. Irrespective of inhibitor addition, corrosion potential in the range of −150–0 mV SCE and polarisation resistance higher than 100 Ω m^2 were measured.

In specimens with chlorides 1.5% or 2.5% by cement weight and inhibitors added with the suggested dosages, potential and polarisation resistance values are much lower. Corrosion potential reached values close to −300 and −400 mV SCE, and polarisation resistance decreased to values lower than 10 Ω m^2, that correspond to corrosion rate higher than 1–2 μm/year, so not negligible. Different behaviour was observed in concrete with 20 L/m^3 calcium nitrite based inhibitor (Fig. 5): polarisation resistance was lower than values measured in chloride free concrete but always higher than 10 Ω m^2, i.e. corrosion rate is low.

Rebars in concrete specimens with chlorides 1% and 1.5% by cement weight and inhibitors in the maximum allowed dosage (as declared by producers) showed polarisation resistance higher than 10 Ω m^2, but lower than in chlorides free concrete (Figs. 4 and 5).

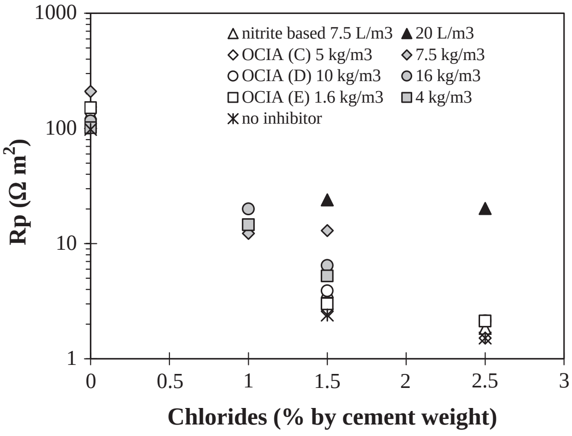

Fig. 5. Polarisation resistance of rebars in concrete specimens with admixed chlorides: mean values between 100 and 500 days of atmospheric exposure. Open symbols: inhibitor dosage suggested by producers. Filled symbols: maximum allowed dosage.

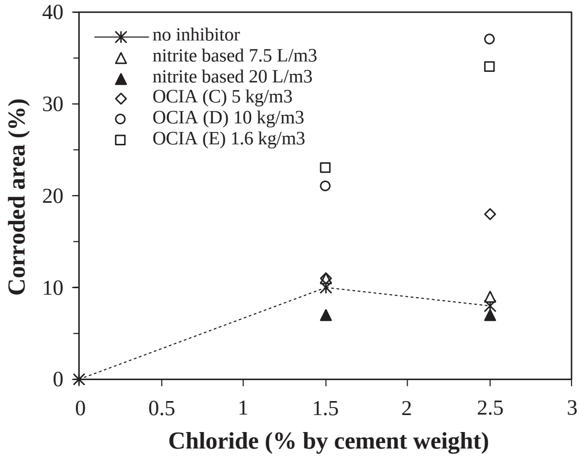

Fig. 6. Percentage of corroded area of carbon steel rebars embedded in chlorides containing concrete after 3 years exposure.

After three years tests, specimens containing chlorides 1.5% and 2.5% were broken for rebars visual inspection and determination of percentage of corroded area, corrosion penetration depth, and mean and maximum penetration rate. All the rebars were deeply corroded in correspondence of the reference electrode fixing strip ("crevice corrosion"), but deep localised attacks ("pitting") were also found far from the reference electrode.

The percentage of corroded area is reported in Fig. 6. The higher the chlorides content, the higher the corroded area. The highest value was measured in concrete with organic inhibitors. Only with nitrite based inhibitor the percentage is lower than 10%, irrespective of chlorides content, according to the anodic mechanism of action of nitrite based inhibitors.

Weight loss measurements confirm polarisation resistance data, as can be seen comparing data reported in Figs. 5 and 7: the higher the polarisation resistance (i.e. the lower the corrosion rate), the lower the specific weight loss. Only nitrite based inhibitor in the maximum allowed dosage significantly reduce the specific weight loss (close to 2–5 mg/cm^2). All the organic inhibitors showed values similar or slightly higher than those measured in the case of rebars in concrete without inhibitors.

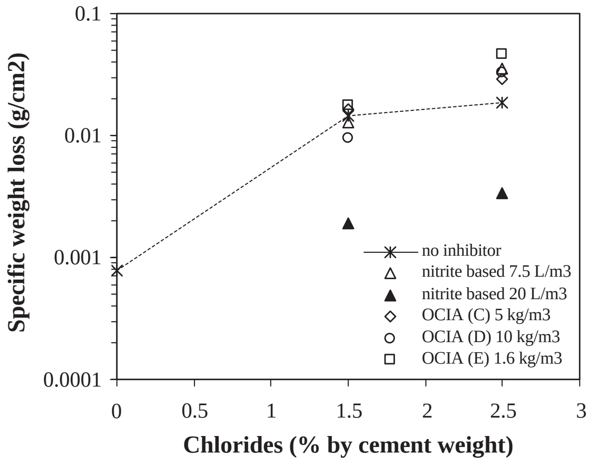

Fig. 7. Specific weight loss of carbon steel rebars embedded in chlorides containing concrete after 3 years exposure.

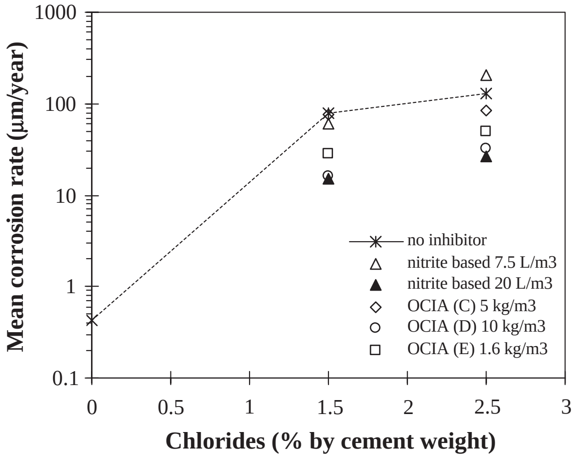

Fig. 8. Mean corrosion rate of carbon steel rebars embedded in chlorides containing concrete after 3 years exposure (calculated by weight loss data and referred to the real corroded area).

Mean penetration rate referred to real corroded area (Fig. 8) is always higher than 10 µm/year, and in some cases higher than 100 µm/year in concrete with maximum chlorides content. The lower values were measured with nitrite based inhibitor at higher dosage and with OCIA-D; nevertheless, obtained values are higher than 10 µm/year, so not negligible.

Maximum penetration in three years tests, evaluated by optical microscopy, ranges from 0.35 to 1.3 mm. By these data, the maximum penetration rate has been evaluated (Fig. 9): minimum value (150 µm/year) corresponds to specimen with nitrite based inhibitor 20 L/m^3 and chlorides 1.5% by cement weight. Maximum penetration rate may be estimated from 200 to 500 µm/year.

3.3. Concrete subjected to chlorides penetration

Three concrete samples, each with one carbon steel rebar, have been cast for every corrosion inhibitor. Rebar free corrosion potential and polarisation resistance trend for all concrete specimens subjected to chlorides penetration are reported in Figs. 10 and 11. Forty-seven ponding cycles, three weeks each,

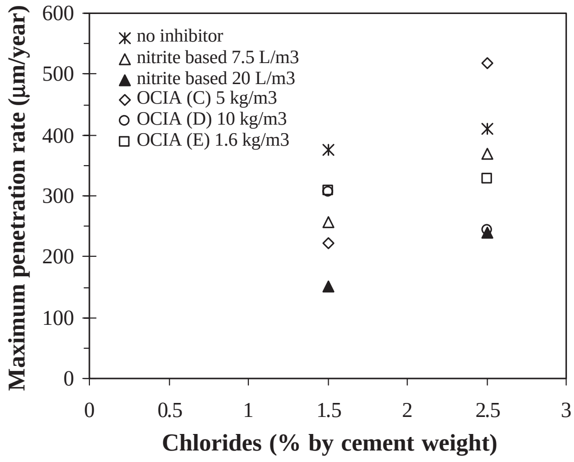

Fig. 9. Maximum penetration rate referred to 3 years exposure (evaluated by optical microscopy).

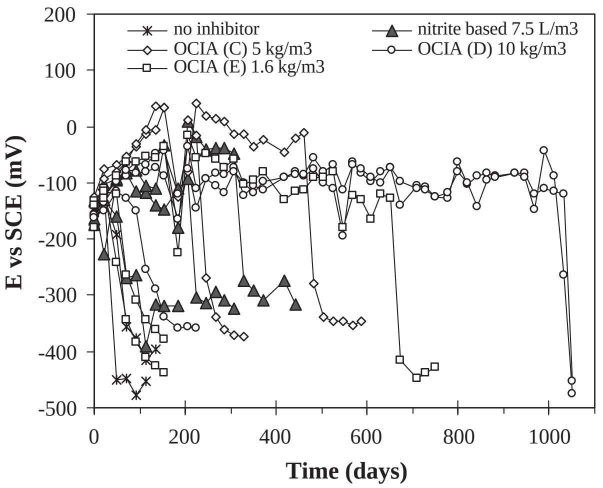

Fig. 10. Free corrosion potential of rebars in specimens subjected to chlorides penetration.

have been performed. In all cases initial rebar free corrosion potential was about −100 mV SCE and polarisation resistance was close to 100 Ω m^2, i.e. rebars were in passive condition. The sudden decrease of potential to values lower than −350 mV SCE indicates the corrosion occurrence (Fig. 10). At the same time, or later, also the polarisation resistance lowered to values in the range of 1–10 Ω m^2. After three years, at the end of the test (6 months later the last measurements reported in Figs. 10 and 11), before rebars visual inspection, all carbon steel reinforcement showed low polarisation resistance, so not negligible corrosion. Considering the potential trend (Fig. 10), some organic inhibitors seem to be able to delay corrosion initiation with respect to the concrete without inhibitors. Organic inhibitor OCIA-D has the best effect, even better than nitrite.

At the 37th ponding cycle (820th day) a core has been taken for each specimen and total chlorides profile in concrete specimens was determined. Chloride profiles were also determined on plain concrete specimens, at the cycle in which corrosion occurred on two of the three reinforced specimens. In all concrete specimens with organic inhibitors, chlorides content is lower with respect to the one measured in concrete without inhibitors (Fig. 12). This effect was also noticed for nitrite based inhibitor, since the commercial mixture contains some organic substances, as reported on its technical sheet. At the rebar level (20 mm) chlorides content is close to 2.1% (±0.01%) by cement weight for concrete without added inhibitor, while it is in the range of 1.2–1.8% in concrete with corrosion inhibitors. At the end of the tests (after 47 ponding cycles) chlorides content at the rebar level was measured in all the reinforced specimens: the lower values were detected in concrete with organic inhibitors (Table 4).

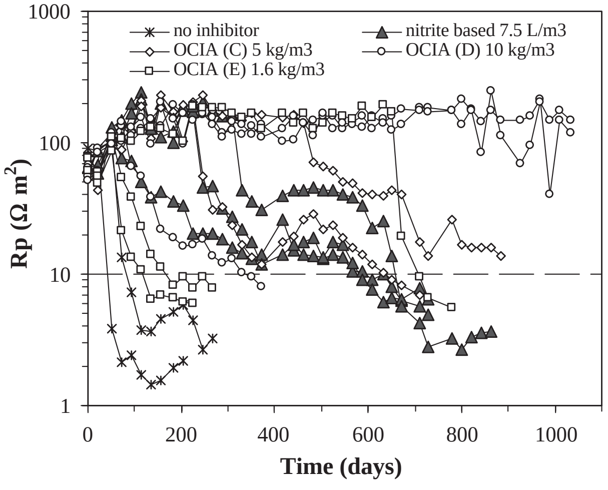

Fig. 11. Polarisation resistance of rebars in specimens subjected to chlorides penetration.

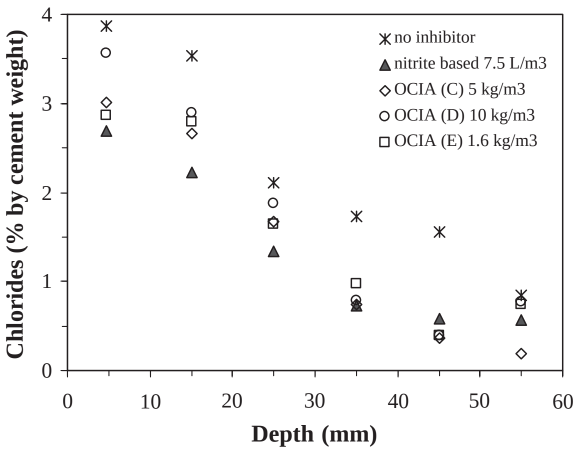

Fig. 12. Total chlorides profiles measured after 37 ponding cycles.

At the end of the tests, concrete specimens were broken for rebars visual inspection, determination of corroded area and evaluation of mean corrosion rate (Table 5). Obviously, extent of corroded area increases with the tests duration. The final maximum corroded area was detected on rebar embedded in concrete with nitrite based inhibitor and organic inhibitor OCIA-C, while the minimum values were measured on rebars in concrete with OCIA-D. Evaluated corrosion rate is always higher than 1 μm/year, so not negligible. The highest values were measured for rebars in concrete with inhibitors OCIA-E, even higher than values obtained for rebar in concrete without inhibitors. Only in the presence of nitrite based inhibitor a certain reduction has been measured.

3.4. Cathodic potentiostatic tests in concrete

Fig. 13 illustrates results of potentiostatic cathodic polarisation tests performed in chlorides free concrete. Three tests were performed from each condition: as similar cathodic curves were obtained, for the sake of clarity, only

Table 4
Total chlorides concentration (percentage by cement weight) at the rebar level at the end of the tests (47th ponding cycle)

	Specimen 1 (%)	Specimen 2 (%)
No inhibitor	3.2	3.8
Nitrite based (7.5 L/m^3)	1.4	1.9
OCIA-C (5 kg/m^3)	1.5	1.8
OCIA-D (10 kg/m^3)	2.0	1.8
OCIA-E (1.6 kg/m^3)	2.5	2.4

Table 5
Percentage of corroded area and mean corrosion rate referred to the real corroded area in specimens subjected to chlorides penetration

	Corroded area (%)			Mean corrosion rate (μm/year)	
	37th cycles (820 days)	At the end (1240 days)			
		Specimen 1	Specimen 2	Specimen 1	Specimen 2
No inhibitor	30	46		6.5	
Nitrite based (7.5 L/m^3)	33	69	62	1.3	4.5
OCIA-C (5 kg/m^3)	43	62		4.4	
OCIA-D (10 kg/m^3)	30	44	29	6.2	7.4
OCIA-E (1.6 kg/m^3)	13	41	52	11.8	8.8

one of them is reported for each different experimental condition. Results are reported as mean cathodic current density in the last 24 h polarisation. Increasing cathodic polarisation the current density increases one order of magnitude, from 4–20 to 80–130 mA/m^2. At −500 mV SCE nitrite based inhibitor and OCIA-C shows the lowest cathodic current density (4–5 mA/m^2). It is important to notice that in the case of nitrite based inhibitor the behaviour in concrete is different with respect to that obtained in solution tests: in concrete slab the measured cathodic current density is the lowest, whereas in solution test was the highest.

4. Discussions

Concerning service life of reinforced concrete structures subjected to corrosion, inhibitors performance will be discussed in terms of ability to influence time-to-corrosion and corrosion propagation time.

4.1. Effect on time-to-corrosion

All the tested inhibitors seem to be able to increase corrosion initiation time in concrete subjected to accelerated chlorides penetration (Fig. 14). Nevertheless, results are scattered. Minimum values of corrosion initiation time in the presence of inhibitors are similar or slightly higher than those observed in the reference specimens, as for example in the presence of inhibitor OCIA-E. Considering the maximum values, inhibitor OCIA-D shows the best effect, while nitrite based inhibitor and OCIA-C behave in a similar way.

The increase of corrosion initiation time can be related to two different effects: reduction of chlorides penetration rate in concrete, or increase of critical chlorides content for the initiation of corrosion. These effects will be separately discussed.

4.1.1. Effect on chlorides penetration

Some authors reported a reduction of chlorides penetration if OCIA are added to the concrete mixture [3,19,35]. This effect cannot be considered a real inhibiting action, since it can be obtained by acting on concrete mixture proportion, reducing W/C ratio or with pozzolanic or blended cements. Nevertheless, compact and adequate concrete cover can have a synergic effect in combination with inhibitors. For example, Berke and other authors have recommended the use of nitrite based inhibitor in combination with low W/C and high concrete cover, not only to prevent leaching of inhibitor [5].

Only for comparison purposes, chlorides profile experimental data (Fig. 12) have been interpolated by means of second Fick's law analytical solution in order to evaluate the effective chlorides diffusion coefficient (D_{ce}) and the chlorides surface concentration (C_s). Results are reported in Table 6. It is confirmed that concrete with organic inhibitors presents lower diffusion coefficient and chlorides concentration with respect to the values obtained in the concrete without inhibitor: diffusion coefficient in specimens contain-

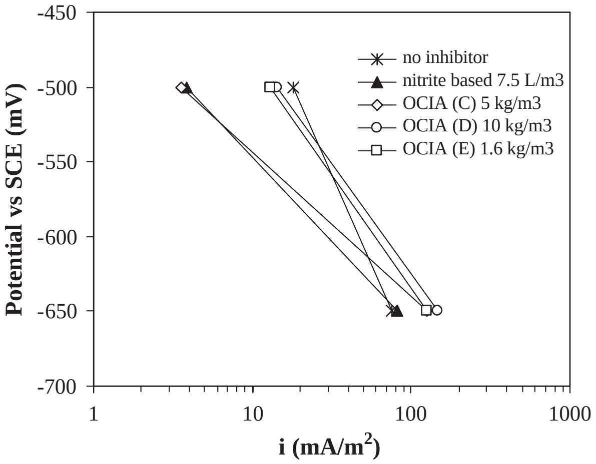

Fig. 13. 48 h potentiostatic polarisation tests in chlorides free concrete: mean cathodic current density in the last 24 h test.

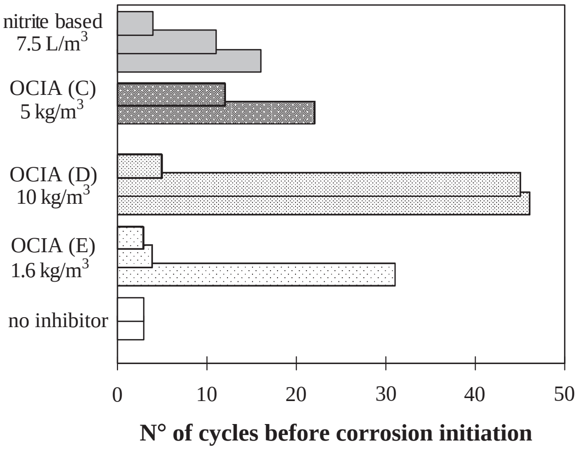

Fig. 14. Corrosion initiation time for specimens subjected to ponding tests with 3.5% NaCl solution.

Table 6
Chloride effective diffusion coefficient (D_{ce}) and surface chloride content by cement weight (C_s) obtained by interpolation of experimental data, reported in Fig. 2, by non-linear regression with second Fick's law

	Chloride profiles measured in plain specimens			Chloride profiles measured in reinforced specimens		
	Ponding cycle	D_{ce} (10^{-8} cm^2/s)	C_s (%)	Ponding cycle	D_{ce} (10^{-8} cm^2/s)	C_s (%)
No inhibitor	4th	14.1	2.8	37th	12.9	4.4
Nitrite based (7.5 L/m^3)	30th	5.5	2.3	37th	7.9	3.1
OCIA-C (5 kg/m^3)	47th	2.4	5.6	37th	6.3	3.7
OCIA-D (10 kg/m^3)	47th	4.7	5.8	37th	6.6	4.2
OCIA-E (1.6 kg/m^3)	6th	10.7	2.8	37th	8.6	3.5

ing inhibitors is from 2 to 4 times lower than that in concrete without inhibitor. Results allow to affirm that all the tested inhibitors show a "physical-barrier" effect, not only OCIA inhibitors, but also nitrite based inhibitor, that contains some organic compounds. This effect is probably due to the formation of complex compounds between organic substances and cement paste that block the pores, reducing chlorides penetration.

It is worth to notice that this effect is less evident if compared to results obtained with pozzolanic or blended cements, able to reduce the diffusion coefficient al least one order of magnitude, or for concrete with lower W/C ratio [44].

4.1.2. Effect on the critical chlorides concentration

Regarding the inhibitors influence on the critical chlorides content for localised corrosion occurrence, nitrite based inhibitor must be analysed separately from organic products. In fact, literature data define a critical chlorides threshold only in the case of nitrite based inhibitor: according to some authors, critical values of $[Cl^-]/[NO_2^-]$ molar ratio range from 0.8 to 1.5 depending on the concrete quality [3–8]. Experimental data are in agreement with literature. On the basis of extrapolated data (Table 6) the chlorides content at the rebar level at the occurrence of corrosion was in between 0.4% and 0.9% by cement weight, that corresponds to a $[Cl^-]/[NO_2^-]$ molar ratio in the range of 1.1–2.0.

In the case of organic inhibitors literature data do not allow to define a critical chlorides content. As reported in the state of the art report by Elsener [3], there is lack of agreement among scientific community in defining the real effectiveness of these inhibitors: conflicting results are reported, it is not well known the composition of the commercial inhibitors and the active substances concentration, there is no clear indication about the inhibitor dosage to prevent corrosion in relation to the chlorides content [3,12–22,32–36]. Probably, due to the mechanism of protection afforded by these compounds (mixed filming inhibitors), the minimum dosage for inhibition should be enough to film the whole rebar surface.

Data obtained in the present research indicate a moderate effect of these inhibitors on localised corrosion initiation. In solution tests, inhibitors OCIA-D and OCIA-E do not affect chlorides content for corrosion initiation (Fig. 2): this is probably related to the evaporation of the active part of the inhibitor mixture, that is a volatile amine, as reported in [3].

More interesting results have been obtained in concrete tests: in this case the inhibitors are expected to remain into concrete. Only inhibitor OCIA-C increases critical chloride in both solution and concrete tests.

Chlorides concentration at the rebar level (Table 7) has been extrapolated using the analytical solution of the second Fick's law (Eq. (2)) considering the diffusion coefficient in Table 5. Critical chlorides content ranges from minimum values, very close to those measured for reference concrete, to maximum values close to 1%, 1.5% and 2% for OCIA-C, OCIA-E and OCIA-D, respectively. These ranges are confirmed also by results in concrete containing chlorides: corrosion occurred when chlorides content was equal or higher than 1.5% by cement weight (Figs. 4 and 5). Only with inhibitor OCIA-C added with the maximum allowed dosage (7.5 kg/m^3) the polarisation resistance is higher than 10 Ω m^2, i.e. corrosion is negligible; nevertheless, lowering of corrosion potential was measured. In specimens with chlorides 1% by cement weight and maximum inhibitor dosage, potential and polarisation resistance showed values intermediate between typical passive and active conditions (Fig. 4). Corrosion rate is negligible, although it is important to point out that tests without inhibitors were not performed in similar conditions, moreover it is well know that for reinforced concrete structures exposed to atmosphere, the critical chlorides threshold is in the range of 0.4–1% [1].

4.2. Effect on corrosion propagation time

The effect of inhibitors on corrosion propagation can be related to the reduction of corrosion rate, due to lower penetration rate or lower corroded area. In any case, concerning the service life of a reinforced concrete structure subjected to chloride-induced corrosion, the conservative approach is to assume the time at which repair actions should be planned (in order to maintain the serviceability of the structures) equal to the initiation time. The period of propagation, which may be of short duration if compared to initiation time, is traditionally not

Table 7
Critical chlorides content at the rebar level extrapolated by analytical solution of the second Fick's law at the cycle of corrosion occurrence

	Chlorides (% cem)
No inhibitor	0.3–0.5
Nitrite based (7.5 L/m^3)	0.4–0.9
OCIA-C (5 kg/m^3)	0.6–1.2
OCIA-D (10 kg/m^3)	1.8–1.9
OCIA-E (1.6 kg/m^3)	1.4–1.6

taken into account because of the uncertainty with regard to the consequences of localised corrosion [1]. However, depending on the limit state and on the actual corrosion rate, the propagation time could be sufficiently long to be considered, at least for economical reasons.

Due to that, the effect of corrosion inhibitors on propagation time seems to be less important than the effect on initiation time.

Only nitrite based inhibitor in the higher dosage lowers corrosion rate (Figs. 5 and 7). Lowest penetration rate, referred to corroded area, was measured for nitrite based inhibitor with high dosage and inhibitor OCIA-D (Figs. 8 and 9). Nevertheless, mean penetration rate referred to corroded area is higher than 10 μm/year (Fig. 8), so corrosion cannot be considered negligible.

In specimens subjected to chlorides penetration, a lowering of corrosion rate after corrosion initiation was observed only in the presence of nitrite based inhibitor (Table 5). In the other cases, corrosion rates range between 4.5 and 12 μm/year. Corroded area increases with test duration; no inhibitors show any significant area reduction with respect to rebars in concrete without inhibitor, except one rebar in concrete with inhibitor OCIA-D. Sometimes also an increase can be noticed (Fig. 6 and Table 5).

It is important to underline that an increase in the extent of corroded area could not be a negative effect if it implies a reduction in the corrosion penetration rate. This was detected on rebars embedded in chlorides containing concrete with organic inhibitors OCIA-D and OCIA-E: corroded area is 2 to 4 times higher than the reference conditions (Fig. 6), but mean corrosion rate and maximum penetration rate are lower (Figs. 8 and 9).

Finally, a comparison between the specific weight loss calculated by integration in time of measured corrosion rate and the specific weight loss measured at the end of the tests has been performed. Results are reported in Fig. 15: it is evident the good correlation between experimental and calculated data. This is not surprising and confirms what is reported in [45].

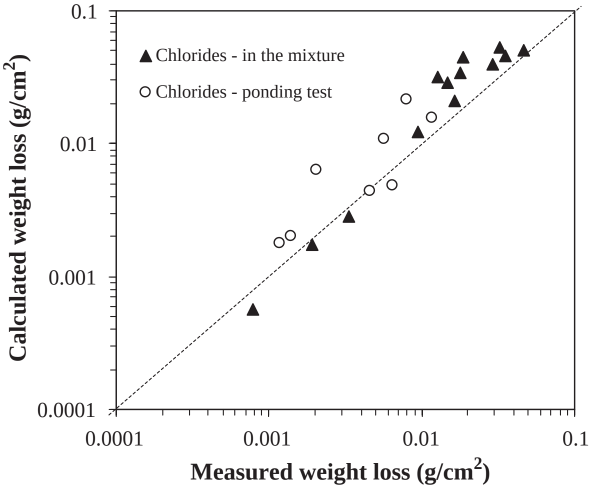

Fig. 15. Comparison between measured and calculated specific weight loss.

4.3. Effect of inhibitors on cathodic process

Potentiodynamic polarisation solution tests showed an increase on the cathodic current in nitrite containing alkaline solution, confirming its anodic oxidising mechanism.

For organic inhibitors, reduction of cathodic current more than one order of magnitude was observed; the effect was more pronounced increasing the inhibitor content (Fig. 3). This seems to be in accordance with the “mainly cathodic” mechanism action reported in literature [3,19]. These results were only partially confirmed in potentiostatic tests performed in concrete (Fig. 13): after 24 h of cathodic polarisation at −500 and −650 mV SCE the measured cathodic current density is not so different with respect to those measured in concrete without inhibitors. Only inhibitor OCIA-C shows a lowering of the current density, but only at −500 mV SCE.

4.4. Mechanism of inhibition

Aim of this experimental research was to evaluate and compare the effectiveness of four corrosion inhibitors, available on market as admixtures for new concrete structures. Taking into account results obtained in three years research, the tested inhibitors are able to delay the onset of chlorides induced corrosion: this is mainly related to a reduction of the penetration rate of chlorides (as suggested by the lower estimated chlorides diffusion coefficient) rather than an increase in the critical chlorides threshold for the occurrence of localised corrosion. It is possible to state that the commercial organic inhibitors reduce the ingress of chlorides by filling concrete pores and blocking the porosity of concrete with the formation of complex compounds. The slight increase in the critical chlorides threshold is not so important, and it seems not always reproducible and also influenced by experimental test condition. Summarising, the inhibitors interact mainly with the cement paste, whereas no significant actions have been measured at the interface with the reinforcement.

To conclude, it must be underlined that, from an electrochemical point of view this effect is not a pure inhibitive action, but it is related to some changes in concrete porosity; a similar or stronger reduction may be obtained using low W/C ratio, or by adding pozzolanic or fly ash cement [1].

5. Conclusions

Based on three years corrosion tests, the main following conclusions can be drawn:

- all the tested inhibitors are able to delay the occurrence of chlorides induced corrosion: this is related to a reduction of chlorides penetration rate in concrete, even if a slight increase on the critical chlorides threshold was observed. The organic commercial inhibitors reduce the ingress of chlorides by filling concrete pores and blocking the porosity of concrete by the formation of complex compounds. Results must be confirmed with further laboratory and field long-term tests;

- results obtained in the presence of nitrite based inhibitor are in agreement with literature;
- no clear and significant effect was noticed on corrosion rate: analysed organic inhibitors seem to reduce the extent of corroded area and the penetration rate, but the reduction is not significant.

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